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SELECTION OF ELECTRODES FOR THE ″IN SITU″ ELECTRICAL RESISTIVITY MEASUREMENTS OF MOLTEN ALUMINIUM

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Abstract

The aim of this paper is the selections of proper electrode material for four-probe technique electrical resistivity measurement of aluminium and aluminium alloys. The biggest problem of electrodes is oxidation during measurement causing high contact resistance and giving wrong results. Various materials have been tested and aluminium electrodes have been chosen. Advantage of aluminium electrodes is that they are melted in specimen right after the pouring and causing no interface which is resulting with any contact resistance. The device together with measuring cell for ″in situ″ measurement of electrical resistivity was developed using four-probe DC technique.

Keywords: *Electrical resistivity; Four-probe technique; Electrode material; Aluminium.*

1. Introduction

Several methods exist for characterization of solidification of metal materials using thermal analysis, metallographic analysis, dilatometry and electrical resistivity measurement described in literature [1-3].

Electrical resistivity measurement is a quite commonly used method for material characterisation. There are several different methods used for measuring electrical resistivity within molten metals, such as inductive techniques, the rotary magnetic field method [4–6] the two-probe method, and the most popular four-probe DC method. The four-probe DC method is used to eliminating the measurement of wires' resistivities and is used for measuring small resistivity. In order to eliminate thermoelectric effects on contacts between electrodes and the sample, the current with very low frequency square wave [7] or bi-directional current [8, 9] is used.

Measuring electrical resistivity within a solid state using a four-probe DC method is not that problematic in terms of measuring cell and contact materials, as the material is in a solid state, a measuring cell for containing sample is unnecessary and there are less reactions between the electrode material and the sample at lower temperatures [10 – 14].

Measurement within a liquid state and during solidification, however, can cause several problems because the metal must be held in measuring cell and the electrode material selected in a manner that achieves good contact and prevents reactions with the melt. Electrode material must be selected in order to prevent oxidation of the electrode prior to immersion within the liquid metal sample. Oxidized electrodes can cause high contact resistance leading to incorrect results. Dissolved electrodes in liquid metal can change the chemical composition of a sample which is influencing electrical resistivity and pour wetting between the electrode and the melt again negatively influences contact resistance, so the wetting should be good [8]. Different authors have used electrodes of several materials, such as tungsten, platinum, molybdenum, graphite, high alloyed stainless-steel and nickel [7 – 9, 15 – 17] for measuring electrical resistivities of different metals. For aluminium and aluminium alloys they used tungsten [17] graphite [15] and stainless-steel [16] electrodes.

All authors have performing measurements in furnaces at controlled temperatures, meaning that they melted the sample, inserted electrodes, and performed measurements during controlled cooling. Their measuring cells were of different shapes and made of different materials, such as ceramics, alumina, and silica. Measuring cells' materials should be selected in order to prevent reactions with the melt, and should not conduct electric current.

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The shape of the measuring cell should also be constructed in such way that specific electrical resistivity can be calculated.

2. Experimental

Measurements were performed on 99.9 wt. % pure aluminium and an aluminium silicon alloy (AlSi9Cu3) where the melt was gravity casted into the measuring cell at approximately 820 °C and then left to cool down untill 50 °C. During cooling the temperature and electrical resistivity were measured continuously.

When selecting a proper electrode material, two different shapes of measuring cells were used from two materials, respectively. The first one was a Croning measuring cell for thermal analysis, and the second block-shaped casting from aerated concrete mould. The castings from these two cells are shown on Figure 1. In the case of selecting electrode material we were disinterested in specific electrical resistivity so we only monitored the shapes of those curves that should have been similar to those in the reference [15] this is when the resistivity is linearly decreasing with the temperature in the liquid state, followed by an instant drop within the solidification range, and again linear decreasing with the temperature in the solid.

The tested electrodes were made from nickel wire, molybdenum wire, copper wire, aluminium wire, and a graphite bar. The temperature was measured using a K-type thermocouple. The four-probe DC technique was used for measuring electrical resistivity. In order to eliminate the thermoelectric effect, the current source was square-waved with an amplitude 0.5 A, the offset being 0.5 A. The current frequency was 1 Hz and the duty cycle of square-wave was 70 %. The voltage was measured using a National Instruments CompactDAQ NI 9219 analogue digital converter, connected to Labview software. The sampling rate was 10 Hz. The voltage, measured when the current was 0 A – U_0 was subtracted from the voltage measured when the current was 1 A - U_u. The thermoelectric effect was eliminated from the resistance measurement using this measurement. The current wave and resistance calculation is presented in Figure 2 and the measuring equipment is shown in Figure 3.

The measuring cell was constructed on the basis of an ABACUS simulation of an electrical field across the sample in order to position the potential electrodes within an area where the current density is homogenous [10]. The material of the measuring cell was calcium silicate brick that can sustain temperatures of up to 1000 °C. The length of the mould cavity from the cell was 220 mm; the cross-section was 295 mm^2 in the shape of a trapeze. Current electrodes were inserted at the ends of the

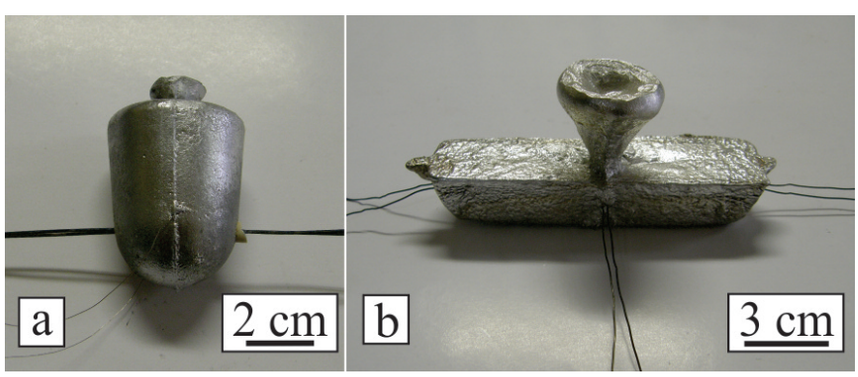

Figure 1. *Casting from the Croning cell with molybdenum electrodes (a) and block shaped-casting from an aerated concrete cell with nickel electrodes on the sides (b) and thermocouples located in thermal centres of castings.*

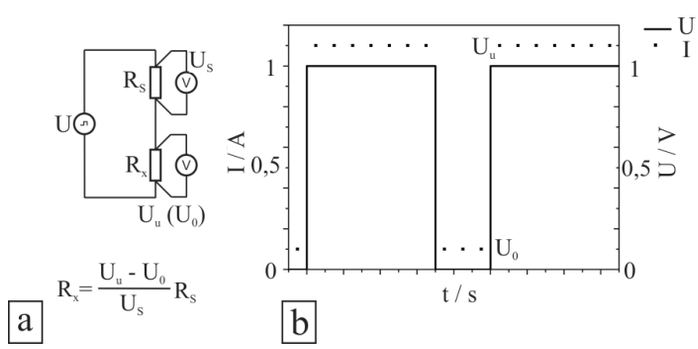

Figure 2. *Measuring scheme with the equation for electrical resistivity (a), and square wave current with measured voltage (b).*

cavity, and the potential electrodes inserted 25 mm from the ends as, shown in Figure 3.

Contacts between the electrodes and the samples were analysed by optic metallography using an Olympus BX 61 microscope, and scanning electron microscopy (SEM) in JEOL JSM-5610. The chemical composition was determined by energy dispersive spectroscopy (EDS).

3. Results and discussion

The result from ABACUS simulation showed a homogenous electrical-field that caused homogenous current density across the casting. It is shown in Figure 4 that homogenous current density was reached approximately 1.5 cm from the current electrode. On the basis of this result the measuring cell from the calcium silicate was constructed, where the potential electrodes were inserted 25 mm from the current electrodes.

During the testing of different electrode materials the graphite, Ni, and Mo showed negative results. The electrical resistivity of the casting rose during the complete measurement, which is not the case regarding the theory in literature [15, 18]. In the case of the graphite bar, the contact between the electrode and the sample was interrupted due to shrinkage of the casting during solidification and cooling. At the same time, it was hard to implement all four electrodes into one measuring cell. At the interface between the Mo and Ni electrodes and the melt, there oxidation of the electrodes occurred because of high temperatures. This oxide-layer caused an increase in contact resistance and was increased the electrical resistivity of the sample during measurement. Figure 5 shows contact of the Ni electrode in the AlSi9Cu3 alloy, where the dark thin-film represents the oxide between the electrode and sample. It was confirmed by the line EDS analysis presented in Figure 5c, and the line of the EDS is marked in Figure 5b.

When the Cu electrodes were tested it was obvious immediately after measurement that the Cu had dissolved in the aluminium because the Cu wires had silver coloured surface near the sample and had broken off because of brittleness. This was because the Al diffused into the Cu. Metallographic analysis of the Al sample with Cu wires is shown in Figure 6 where the Cu phase Al_2Cu – Θ (according to literature [19]) is seen within the area of contact. In addition the area of the Cu wire is marked in the Figure although it was mostly dissolved in the Al sample. It can be seen from these findings that the contact between the wire and the

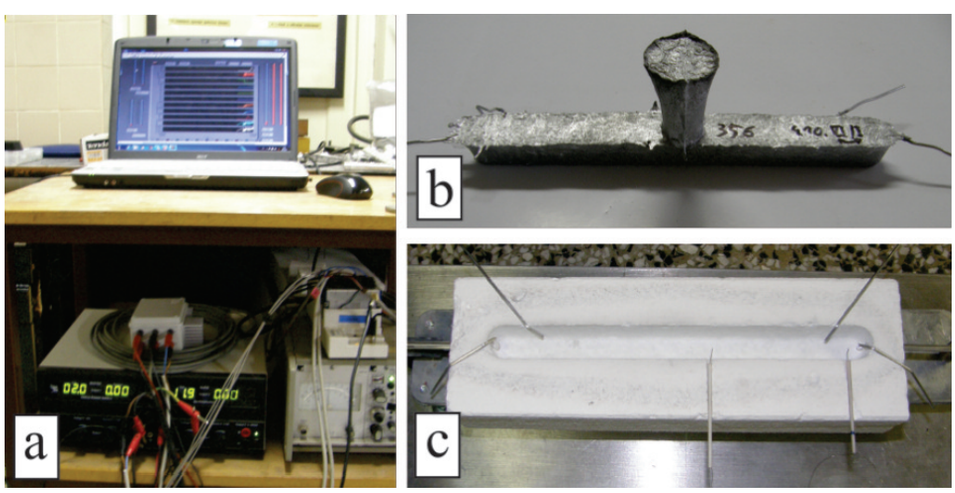

Figure 3. *Complete device for measuring electrical resistivity and temperature (a), casting from a calcium silicate measuring cell (b), and the measuring cell with electrodes and two K-type thermocouples inserted.*

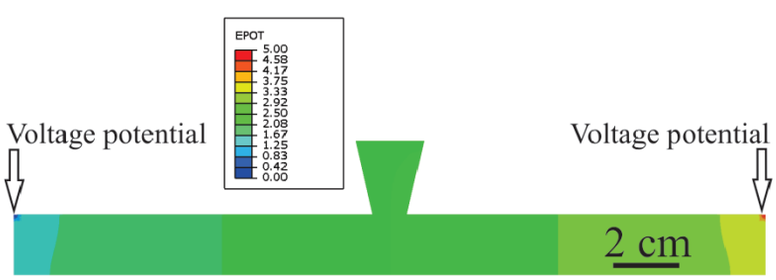

Figure 4. *Result from ABAKUS simulation of the electrical-field.*

sample was eliminated by fusing Cu wire with the Al sample consequently eliminating the contact resistance too. Dissolution of Cu in the sample is inconvenient because the sample is then contaminated by Cu atoms, thus leading to a higher electrical resistivity of the sample. In order to avoid contaminating the sample with impurities, Al wires were used which are similar as Cu wires, molten and dissolved in the specimen, thus eliminating contact resistance. Metallographic investigation of the samples using Al wires are presented in Figure 7 where the positions of the wires are marked. Figure 7a shows the Al sample with the Al electrode, where it can be seen that the outer surface of the Al wire is not totally molten but the inner part of the wire is well fused with sample. Figure 7b shows the AlSi9Cu3 sample with the Al electrode, where the electrode's fusion within the sample can be clearly seen. The fused area has finer eutectic due to a higher cooling-rate during solidification after Si was diffused into the wire. Such a contact of the Al wire with the sample of pure Al or Al alloy is ideal because the contact resistance is eliminated and sample is not contaminated with impurity atoms, but is just diluted by Al.

Testing of the constructed measuring cell showed good results. The electrical resistivity of the Al sample changed during cooling and solidification, in the order as described in the literature. The result from the measurement is presented in Figure 8b. It can be clearly seen that the results are completely comparable to those of Brandt and Neuer [15], as shown in Figure 8a.

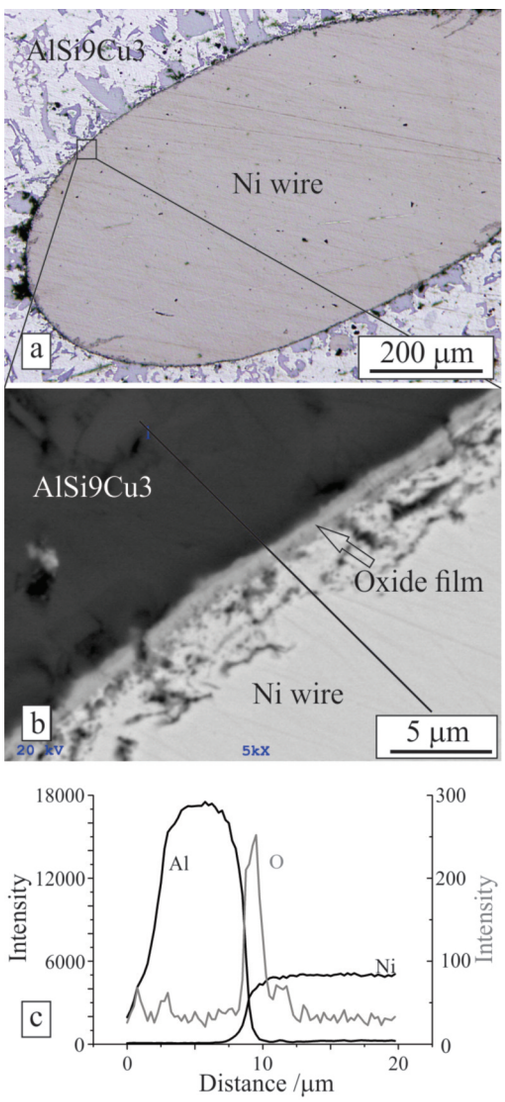

Figure 5. *Contacts of the AlSi9Cu3 sample with Ni wire: optic micrograph (a), SEM micrograph (b) and line EDS analysis (c).*

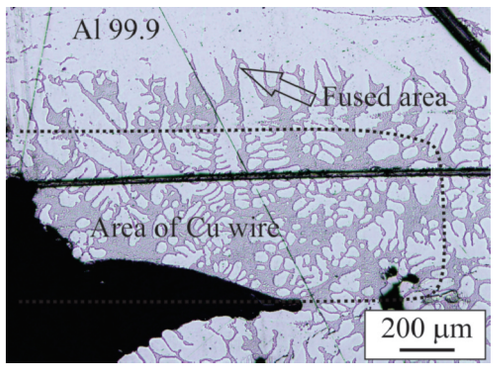

Figure 6. *Optic micrograph of Al sample with Cu wire.*

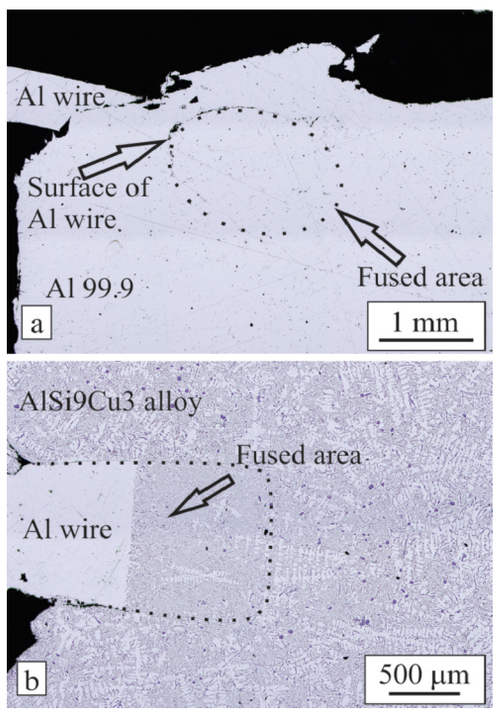

Figure 7. *Optic micrograph of Al sample with Al wire (a) and AlSi9Cu3 sample and Al wire (b).*

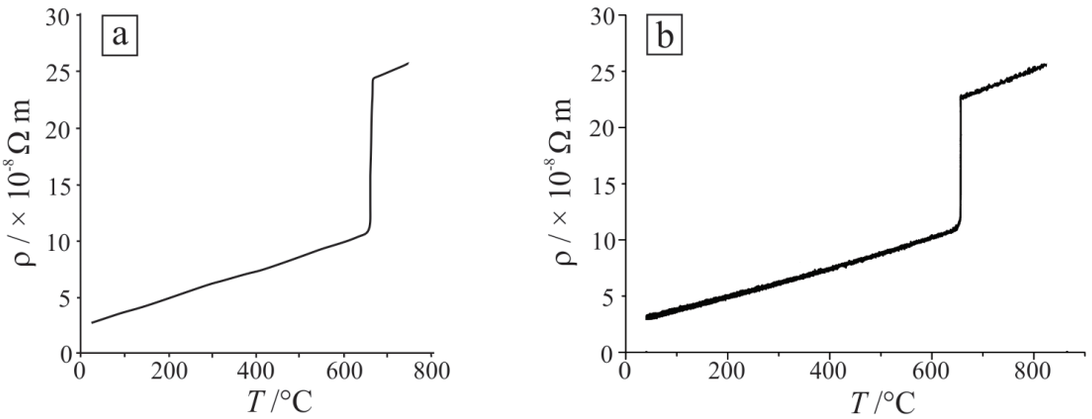

Figure 8. *Specific electrical resistivity of the pure aluminium according to the literature [15] (a) and ″in situ″ measurement of the specific electrical resistivity of the Al 99.9 sample (b).*

4. Conclusions

The conclusions of this work are that the Mo and Ni electrodes are not suitable when measuring the electrical resistivity of molten metals. Oxidation is a common reaction at high temperatures and causes non-conductive layers on the surfaces of the electrodes resulting in an increase in contact resistance. The graphite bars are also not appropriate because of its size and difficulties at implementing them into measuring cell and interruption of contact because of shrinking of casting. The most ideal material for selection is the Al electrode because the wire melts within the molten Al or in the Al alloy, thus creating perfect contact without any contact resistance, and contamination of the sample by impurity atoms.

According to simulation a permanent measuring cell from calcium silicate brick cell was constructed in which ″in situ″ measurements can be performed. The measured specific electrical resistivity of the Al sample coincided perfectly with the measurements from the work of Brandt and Neuer [15].

Reference

[1] P. Mrvar, M. Trbižan, J. Medved, Livarski Vestnik, 48 (5/6) (2001) 131-140.

[2] G. Klančnik, J. Medved, J. Min. Metall. Sect. B-Metall., 47 (2) B (2011) 179 – 192.

[3] S. Kores, M. Vončina, B. Kosec, J. Medved,Metalurgija 51 (2) (2012), 216-220.

[4] S. G. Teodorescu, R.A. Overfelt, S. I. Bakhtiyarov, Int. J. Thermophys., 22 (5) (2001) 1521-1535.

[5] L. Brinker, M. Baenitz, Quantum States, 7 (1998) 2-7.

[6] G. Lohöfer, Meas. Sci. Technol., 16 (2005) 417-425.

[7] J.B. van Zytveld, J. Phys., 41 (8) (1980) 503-506.

[8] B. J. Monaghan, Int. J. Thermophys., 20 (2) (1999) 677-690.

[9] M. Brunčko, A.C. Kneissl, B. Kosec, G. Lojen, I. Anžel, Int. J. Mat. Res. 98 (2) (2007) 1-5.

[10] H. R. Kokabi, Rev. Sci. Instrum., 64 (6) (1993) 1549-1553.

[11] S. Abis, G. Riontino, Phys. Stat. Sil., (a) 114 (1989) 511-518.

[12] G. Riontino, Mater. Sci. Eng., A179/A180 (1994) 323-326.

[13] E. Cadirli, H. Kaya, A. Gümüs, I. Yilmazer, J. Mater. Eng. Perfor., 15 (4) (2006) 490-493.

[14] M. Bizjak, L. Kosec, B. Kosec, I. Anžel, Metalurgija 45 (4) (2006) 281-286.

[15] R. Brandt, G. Neuer, Int. J. Thermophys., 28 (5) (2007) 1429-1446.

[16] L. Moraru, Czech. J. Phys., 49 (2) (1999) 253-261.

[17] G Manchang, J. Jun, L. Quingchun, G. Wenquan, Trans. Nonferrous Met. Soc. China, 7 (4) (1997) 67-71.

[18] A.R. Sinigoj, Basics of Electromagnetics, Publisher of Faculty of Electrical engineering and Faculty for Computer and Information Science, Ljubljana, 1999, p. 169 (in Slovenian).

[19] L. Backerud, G. Chai, J. Tamminen, Solidification characteristics of aluminium alloys: Vol 2: Foundry alloys, University of Stockholm, Stockholm, 1990, p. 45-69.